

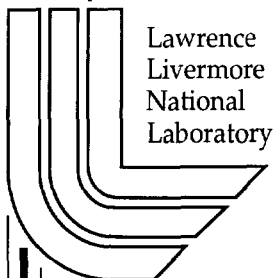
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ELECTRONIC EXCITATIONS AND CHEMISTRY IN NITROMETHANE AND HMX

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Abstract. The nature of electronic excitations in crystalline solid nitromethane under conditions of shock loading and static compression are examined. Density functional theory calculations are used to determine the crystal bandgap under hydrostatic stress, uniaxial strain, and shear strain. Bandgap lowering under uniaxial strain due to molecular defects and vacancies is considered. In all cases, the bandgap is not lowered enough to produce a significant population of excited states in the crystal. Preliminary simulations on the formation of detonation product molecules from HMX are discussed.

INTRODUCTION

The last two decades have produced significant new insights into the basic science of high explosives. Experiments and theory have suggested that the sensitivity of high explosives to initiation by mechanical perturbations or shocks is a strong function of solid-state properties including crystal structure, defects, and dislocations.¹⁻⁵ Behind a shock front lies a region that is far from equilibrium, where solid-state properties may determine the rates and mechanisms through which the material reaches equilibrium.

Chemistry is thought to begin to occur on a 10 or 100 picosecond time scale behind a shock front in some energetic materials.¹ This requires a fast mechanism of energy transfer from the shock wave to the molecular degrees of freedom. A mechanism for energy transfer from the shock directly into molecular electronic degrees of freedom is appealing because electronic excitation to an unstable energy surface can result in rapid dissociation of a molecule. A similar mechanism has been found to be a cause of rapid migration of interstitials in crystalline silicon subjected to radiation.²

In this work we examine mechanisms of electronic excitations by a shock wave in solid nitromethane. Nitromethane is one of the simplest model energetic materials. Nitromethane is in the liquid state at room temperature and pressure, but most practical energetic materials are in a solid state under these conditions. We have chosen to study the crystalline form of nitromethane in analogy with other energetic materials. In particular, we study the effect of the conditions found in a shock or detonation wave on the bandgap of the solid.

COMPUTATIONAL DETAILS

Density functional theory calculations were performed using the PW91³ and PBE⁴ generalized gradient approximations (GGAs) of Perdew. These exchange-correlation functionals produced nearly identical results in comparison cases. Calculations utilized Troullier-Martins pseudopotentials⁵ and Vanderbilt ultrasoft pseudopotentials.⁶ Plane waves with kinetic energy cutoffs of 25 Rydbergs and 40 Rydbergs were used with the Vanderbilt and Troullier-Martins pseudopotentials, respectively. Results obtained using the two sets of pseudopotentials are in good agreement. All

calculations were converged with respect to k-point spacing in the Brillouin zone. In many cases, a single k-point was sufficient due to the minimal amount of dispersion across the single particle bands. Stresses reported here were calculated using an analytic approach based on plane-wave basis functions.⁷

The primitive cell of nitromethane at zero pressure contains four molecules. The atomic positions have been relaxed within the experimental lattice parameters. The space group is $P2_12_12_1$ with orthorhombic lattice vectors $a=5.1832$ Å, $b=6.2357$ Å, and $c=8.5181$ Å at $T=4.2$ K.⁸ Adjacent molecules along the c axis have alternating nitro and methyl groups which gives the unit cell a neutral overall dipole moment.

The calculated bandgap for the crystal at zero pressure is 3.28 eV. The HOMO-LUMO gap for a single molecule is 3.75 eV. This is similar to the 3.8 eV HOMO-LUMO gap for a single molecule calculated using multi-configuration self-consistent field (MCSCF) techniques by Manaa, *et. al.*⁹

While bandgaps calculated within the LDA are typically a factor of two less than experimental values,¹⁰ we believe the gaps presented here to be more accurate for the following reason. One of the assumptions associated with DFT quasiparticle energies is that removal or addition of a particle to a state leaves the total density unchanged.¹⁰ The HOMO and LUMO states of a nitromethane molecule are both localized to the atoms in the nitro group, which results in a relatively minor change in the total density when an electron is transferred from the HOMO to the LUMO. Therefore, the other occupied states do not require significant adjustments since the Kohn-Sham Hamiltonian is a functional only of the total density.

STATIC CONDITIONS

In regions sufficiently far behind the shock front for the stress tensor to be equilibrated, a condition of hydrostatic compression exists. Starting at the experimental atmospheric pressure lattice size, the unit cell was compressed up to a hydrostatic pressure of 180 GPa with 6 intermediate pressure points. At each pressure, the lattice vectors and atoms in the unit cell were relaxed according to the forces. In the pressure range explored, the crystal structure maintained the $P2_12_12_1$ symmetry. No bond bending was observed, but the 180 GPa

molecules have bond lengths shortened by 7-15%. A phase transition of the methyl group rotation angle was observed to occur between the 10 and 30 GPa calculations. Such a transformation has been observed experimentally at 3.5 GPa.¹¹ It is possible that the zero pressure orientation of the hydrogens is only metastable in the 10 GPa calculation. There is also experimental evidence for a structural phase transition at 7 GPa at higher temperatures,¹² but a spontaneous phase transition was not observed in the calculations. The $P2_12_12_1$ structure is at least metastable in this pressure range at zero temperature.

Figures 1 and 2 contain band structures at 2 GPa and 180 GPa, respectively. The bands at low pressure are relatively flat compared to high pressure where dispersion plays a role. As the pressure increases, band dispersion first appears in the mid-valence range, leaving the HOMO state relatively flat. This result is most likely associated with the extended nature of the states in this range. These states are delocalized over the whole molecule, while the HOMO state is localized on the nitro group. Intermolecular interactions should have a greater effect on orbitals that extend over the entire molecule, since they have larger overlaps than localized orbitals.

The bandgap change as a function of pressure is given in Figure 3. The HOMO-LUMO gap of a single molecule in the geometry of the 180 GPa calculation was found to be 3.96 eV using MCSCF techniques.¹³ This indicates that condensed phase effects are important in producing the band gap reduction as a function of pressure. The detonation pressure and temperature of nitromethane has been experimentally determined to be about 13 GPa and 2000 K respectively,¹⁴ and there is not a significant change in the bandgap in the vicinity of this pressure. Even compressing the crystal to a pressure an order of magnitude higher than that observed in developed detonation waves results in a bandgap lowering to around 2 eV, which is not sufficiently low to provide a significant thermal conduction band population at the observed temperatures.

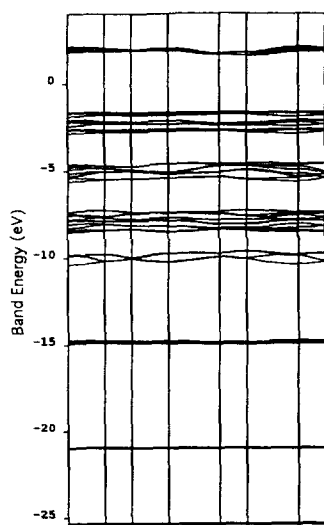


FIGURE 1: The band structure of nitromethane at zero pressure.

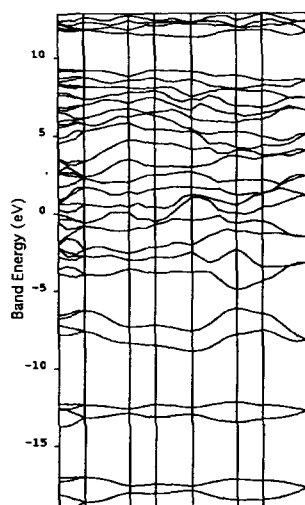
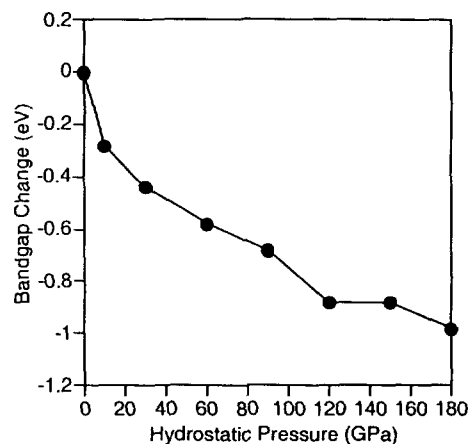


FIGURE 2: The band structure of nitromethane at 180 GPa.

Before the crystal relaxes to a state of hydrostatic stress, a state of uniaxial strain exists immediately after the shock front passes. This uniaxial strain state may last for picoseconds or much longer, depending on the timescale for plastic deformation. The relaxation from this strain state may involve shearing along crystal slip planes or shear wave propagation.

FIGURE 3: The bandgap of nitromethane as a function of



hydrostatic pressure.

The unit cell at zero pressure was uniaxially strained along each of the three lattice vectors and the molecules within the cell were relaxed at each strain state. Uniaxial strain destroys the $P2_12_12_1$ symmetry in cases of extreme strain. We found no significant distortion of the molecular bond angles, although the molecules have reoriented. There was no significant orientational dependence as a function of the strain axis. With the uniaxial strains associated with detonation around 0.2, the bandgaps are lowered to 3 eV.

If we move closer to the shock front, the molecules may have insufficient time to reorient to relax the uniaxial strain. Shock compression without relaxation can be modeled by simply translating the molecules toward each other in the direction of uniaxial compression. This simplistic approach is intended to capture some of the dynamics of the compression in a static calculation.

Figure 4 shows the bandgap change as a function of compression without relaxation along each of the three lattice axes. The data indicate an orientational dependence, with the largest bandgap lowering occurring for compression along the c axis. Compression along this axis brings the nitro groups closer to methyl groups of neighboring molecules. In particular, it brings a hydrogen on one molecule directly toward an oxygen on a neighboring molecule. Compression along the other directions does not bring close contact atoms on neighboring molecules directly towards each other. We expect this transient effect to be very short lived because

the energy barrier for methyl rotation is only 170K at atmospheric pressure. This effect will be addressed in more detail in the section on dynamical effects. It is interesting to note that the a axis is a nearest neighbor direction while the b axis is not, yet the bandgap behavior as a function of compression is nearly identical for these two axes. This is likely due in part to the localization of the HOMO and LUMO states to the nitro group.

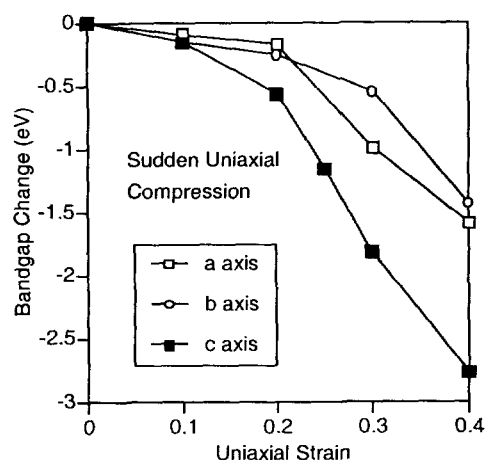


FIGURE 4: The bandgap change of nitromethane as a function of sudden uniaxial strain.

D. Molecular defect

It has been suggested that defects in molecular crystals are sites where increased gap lowering can occur under pressure. We consider, as a simple defect, a flipped molecule in the unit cell. The motivation for this defect is to increase the interactions between HOMO and LUMO states of the flipped molecule and HOMO and LUMO states of a neighboring molecule by bringing them closer together. In this defect configuration, the periodic boundary conditions create an infinite row of molecules along the c axis direction with neighboring nitro groups.

This structure was compressed uniaxially and relaxed, with bandgap change results in Figure 5. The molecular geometries upon compression are within 2-3% percent of the zero pressure values, with little or no bond distortion. The bandgap for the unstrained unit cell is about 3.0 eV, which is 0.3 eV lower than that of the perfect crystal. The bandgap decreases more quickly with uniaxial

strain than it does for the perfect crystal, particularly at high strains. However, the bandgap still does not lower enough to produce a significant population of molecular excited states.

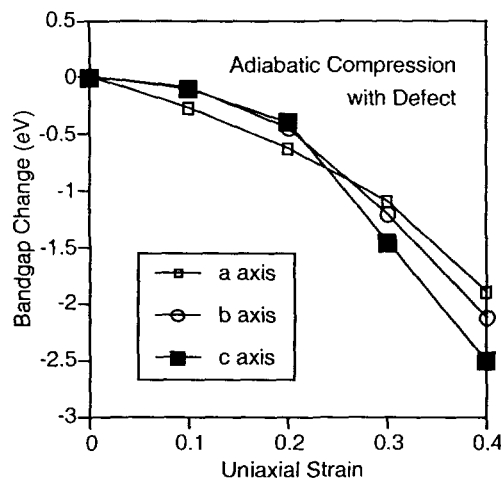


FIGURE 5: The bandgap of nitromethane with a rotated molecule defect.

We can qualitatively summarize the results of all of the static calculations presented here with two points. The bandgap is not lowered enough to create significant thermal populations of excited states under static conditions with strain states comparable to or greater than those of detonation. Also, upon compression and relaxation, the molecules find a way to rearrange to maintain molecular geometries close to their zero pressure values. These two points suggest that if significant bandgap lowering is to occur, molecular bond distortion is required.

DYNAMICAL EFFECTS

Our results indicate significant bond distortion in nitromethane requires the inclusion of dynamical effects. Once the molecules are uniaxially compressed by the shock, they rearrange to their relaxed geometries. We modeled this process for a rapid shock compression along the c axis by doing constant energy *ab-initio* molecular dynamics starting with a unit cell with the molecules translated toward each other. The unit cell was also strained 0.2 along the c axis to reproduce the

uniaxial strain associated with a roughly 13 GPa detonation wave. The internal temperature of the molecules was initially at $T=0$, with no vibrational energy

We performed simulations by colliding molecules along the three unique nearest-neighbor directions in the crystal. Collisions along the [100] and [221] lattice directions were accomplished using an 8 molecule supercell with the length of the a axis doubled.

Collisions along all three directions were calculated for collision velocities between 2 km/sec and 6 km/sec (between 0.02 Å/fs and 0.06 Å/fs). A 1 fs time step was used for the 2km/sec calculations and 0.5 fs was used for the higher collision velocities. All simulations were run for around 100 fs. The maximum observed changes in the HOMO-LUMO gaps as a function of collision velocity are given in Figure 6. This gap minimum was obtained near the peak of the collision in all cases. Figure 6 indicates that the bandgap can be significantly effected at higher collision velocities, but it is still too large for a significant thermal population of excited states to exist.

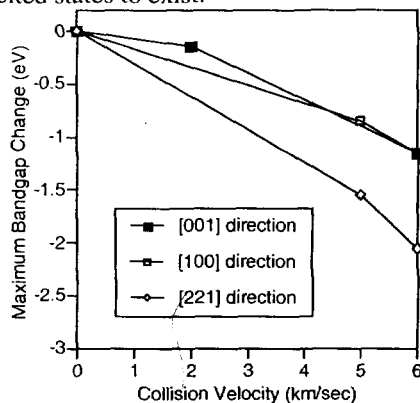


FIGURE 6: The maximum bandgap change found during collisions.

A molecular collision of 10 km/sec along the c direction was considered. This collision resulted in immediate rupture of the CN bond. The formation of new species lowered the bandgap 1.4eV. At the larger collision energies, energy sufficient for bond breaking may be directly channeled into bond breaking modes. This eliminates the need for a fast excited state decomposition mechanism.

HMX DECOMPOSITION CHEMISTRY

In this section we turn our attention to the formation of simple detonation products from high explosive molecules. A preliminary set of quantum molecular dynamics simulations have been performed with an ab initio based tight binding method. In the simulations, a sample of 6 HMX molecules were initially placed in the delta phase. Constant volume and temperature molecular dynamics was performed at a density of 1.9 g/cc and a temperature of 3500K. The total simulation time was 30 ps. These conditions roughly correspond to conditions in the neighborhood of the Chapman-Jouget state of HMX.

The formation of simple detonation product molecules was monitored by identifying bonded atoms throughout the simulation. This identification was made on the basis of bond distances. In Figure 7 we show the number of H₂O molecules found during the simulation. The concentration was fit to a simple exponential function, although some evidence of a decrease in the concentration at times greater than 20ps is seen.

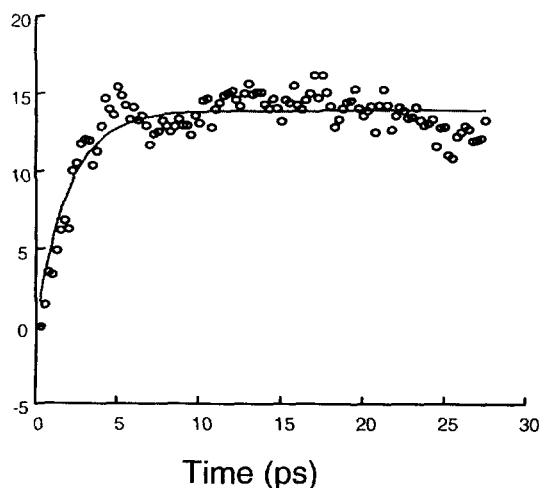


FIGURE 7: Number of H₂O molecules formed during the simulation.

A similar analysis was performed for CO₂, CO, and N₂. Rough values for reaction rates were found by fitting each concentration vs. time plot to a simple exponential. In this way we found a rate of 0.5 ps⁻¹ for H₂O, 0.16 ps⁻¹ for CO₂, 0.12 ps⁻¹ for CO, and 0.05 ps⁻¹ for N₂. More complete future work along these lines will determine reaction rates at several thermodynamic states. Our eventual goal is

a working chemical kinetic model for the formation of detonation products from high explosives.

DISCUSSION

The work of Manaa, *et. al.*, suggests extreme molecular distortions are required to close the HOMO-LUMO gap in nitromethane. However the intermolecular interactions in nitromethane are probably too weak to allow for such significant covalent bond distortion within the molecules under static conditions.

If bandgap closure does occur, it is most likely to be the result of dynamical effects that may occur around defects and vacancies or during shearing of the molecular crystal. The HOMO-LUMO gap decreases observed at high velocities in the dynamical simulations were much more significant than the bandgap decreases for the perfect crystal under realistic static conditions. These dynamical bandgap changes were comparable in magnitude to the molecular defect bandgap changes for large values of uniaxial strain. Perhaps dynamical effects which involve high velocity collisions between the nitro groups of defect molecules are one of the most likely sources of electronic excitations.

The work of Manaa, *et. al.*, suggests roughly 3eV must be channeled into the CNOO bending mode for the HOMO-LUMO gap to significantly decrease. With temperatures associated with detonation in the 0.2 eV range, this can only occur in regions far from equilibrium where energy from the shock has good coupling into this mode. It may, however, be possible for molecular decomposition to occur before such extreme energies are possessed in any single molecular degree of freedom. For example, an energy of 3eV in the CN stretching mode will result in dissociation of the methyl and nitro groups.⁹

Some speculation may be made about the role of electronic excited states in the detonation of other high explosives like TATB and TNT. These molecules are larger than nitromethane and may have fundamentally different electronic structures. If the HOMO and LUMO states are localized on the nitro groups, as in nitromethane, then we would not expect significant bandgap lowering to occur under compression or around defects. Larger molecules may, however, be more susceptible to bond bending during shearing processes than nitromethane due to the lack of a single freely rotating methyl group

which adjusts to relieve molecular strain on the whole molecule.

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